Synthesis of \(N,N,N',N'\)-tetraalkylbenzidines through oxidative coupling of \(N,N\)-dialkylanilines induced by SbCl\(_5\)

Paola Vitale\(^{a,b}\) *, Leonardo Di Nunno\(^{a,b}\) and Antonio Scilimati\(^{b}\)

\(a\) C.I.N.M.P.I.S., Università degli Studi di Bari “A. Moro”, Via Orabona 4, 70125 Bari, Italy

\(b\) Dipartimento di Farmacia, Università degli Studi di Bari “A. Moro”, Via Orabona 4, 70125 Bari, Italy

E-mail: paola.vitale@uniba.it

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Abstract

The oxidative coupling to \(4,4'-N,N,N',N'\)-tetraalkylbenzidines is the main reaction observed during a study on the reactivity of \(N,N\)-dialkylanilines with SbCl\(_5\). A possible reaction mechanism is presented and discussed in comparison with the \(N,N\)-dialkylanilines oxidative coupling achieved with other Lewis acids.

**Keywords**: SbCl\(_5\), oxidative coupling, \(N,N\)-dialkylanilines, \(4,4'-N,N,N',N'\)-tetraalkylbenzidines, photoconductors oLEDs

Introduction

Antimony pentachloride reacts with monoalkylbenzenes or deactivated aromatic compounds, providing an aromatic chlorination by electrophilic aromatic substitution either as a direct chlorinating agent,\(^1\text{-}^5\) or as a catalyst of the chlorination with chlorine gas,\(^6\) because of the combination of its Friedel-Crafts catalytic activity and its oxidation-reduction potential. Some hypotheses have been proposed to explain the higher aromatic paral/ortho-chlorination ratio observed with SbCl\(_5\), in comparison to the reactions with Cl\(_2\)/SbCl\(_5\), a bulky electrophilic species (SbCl\(_4^+\)/SbCl\(_6^+\)) being postulated in the former case.\(^1\text{-}^7\text{,}^8\)

At variance with the above mentioned substrates, no studies on the reactivity of SbCl\(_5\) with anilines or other arylamines were carried out. During the study of some \(N,N\)-disubstituted anilines,\(^9\) we undertaken an investigation on the reactivity of a wide number of substituted benzenes in the presence of Lewis acids, and we found that after treatment of \(N,N\)-dialkylanilines with SbCl\(_5\), followed by neutralization with a base, \(N,N,N',N'\)-tetraalkylbenzidines can be isolated in fair to good yields from the reaction mixture.
Interestingly, in the used experimental conditions, SbCl₅ does not seem to react with anilines as a direct chlorinating agent, and \(N,N,N',N'-\)tetraalkylbenzidines were the main reaction products.

Since substituted benzidines are interesting and useful compounds, for their application in the field of organic solar cells, photoconductors, oLED and other devices, we found interesting to investigate in detail such a new synthetic methodology to \(N,N,N',N'-\)tetraalkylbenzidines.

**Results and Discussion**

We found that the treatment of \(N,N\)-disubstituted anilines 1a-d with SbCl₅, followed by neutralization with a base (aqueous KOH or K₂CO₃), afforded \(N,N,N',N'-\)tetraalkylbenzidines 2a-d in fair to good yields, together with little amounts of chlorinated products (Scheme 1 and Table 1). The formation of insoluble red-brown powders (named from now on, solids 3a-c) was observed in the course of all reactions after SbCl₅ addition to the \(N,N\)-disubstituted aniline solution in CH₂Cl₂. However, some efforts aimed at the isolation of such intermediates in solid crystalline form, from the reaction mixture before the final basic treatment, failed.¹⁰

\[
\begin{align*}
1\text{a-d} & \xrightarrow{1) \ \text{SbCl}_5, \text{CH}_2\text{Cl}_2, 24\text{h}} \xrightarrow{2) \ \text{aq K}_2\text{CO}_3} 2\text{a-d}
\end{align*}
\]

**Scheme 1.** Products of reaction of \(N,N\)-dialkylanilines 1a-d with SbCl₅.

**Table 1.** Products of reaction of \(N,N\)-dialkylaniline (1a-d) with SbCl₅/CH₂Cl₂

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Yield 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Me</td>
<td>2a (81)</td>
</tr>
<tr>
<td>1b</td>
<td>Et</td>
<td>2b (84)</td>
</tr>
<tr>
<td>1c</td>
<td>i-Pr</td>
<td>2c (63)ᵇ</td>
</tr>
<tr>
<td>1d</td>
<td>-(CH₂)₄⁻</td>
<td>2d (38)</td>
</tr>
</tbody>
</table>

*aReaction conditions: SbCl₅/C₆H₅NR₂ (1:1 ratio) were stirred for 24 h under nitrogen atmosphere before treatment with K₂CO₃ (See Experimental). In this conditions SbCl₅ does not react with anilines as a direct chlorinating agent, and \(N,N,N',N'-\)tetraalkylbenzidines were the main reaction products.*

*bThe 3-chloro-\(N',N',N',N'-\)tetraisopropylbiphenyl-4,4'-diamine 2e was also isolated in 35% yield.*
Oxidative coupling of $N,N$-dialkylarylaines to benzidines is a known reaction, and the formation of $4,4'$-$N,N,N',N'$-tetraalkylbenzidines by reaction of $N,N$-dialkylanilines with some transition metals (CAN, TiCl$_4$, etc.) has also been reported. In particular, to explain the oxidative coupling observed in the reaction of $N,N$-dialkylarylaines with TiCl$_4$, a stepwise mechanism has been proposed, that involves the formation of two complexes with TiCl$_4$ (adduct $1_{\text{N-Ti}}$ and $1_{\text{C-Ti}}$), followed by the conversion of $1_{\text{C-Ti}}$ into a radical cation intermediate (Scheme 2).

![Scheme 2](https://example.com/scheme2.png)

**Scheme 2.** Mechanistic hypothesis of $4,4'$-$N,N,N',N'$-tetraalkylbenzidines formation by oxidative coupling of $N,N$-dialkylanilines in the presence of TiCl$_4$.

However, a similar mechanism could not to be proposed when SbCl$_5$ was used, since a very unusual oxidation number +4 should be required for the Sb species (SbCl$_4$) detachment in this case (Scheme 3).

![Scheme 3](https://example.com/scheme3.png)

**Scheme 3.** Mechanistic hypothesis of $4'$-$N,N,N',N'$-tetraalkylbenzidines formation by radical oxidative coupling of $N,N$-dialkylanilines in the presence of SbCl$_5$. 
So, we propose an alternative mechanistic hypothesis (Scheme 4), where the dimerization is just the result of a direct interaction between the starting \(N,N\)-dialkylaniline and the \(1_{N-Sb}\) adduct. Based on this hypothesis, the formation of the \(1_{C-Sb}\) intermediate depicted in Scheme 3 should be excluded.

![Scheme 4](image)

**Scheme 4.** Mechanistic hypothesis of oxidative coupling of \(N,N\)-dialkylanilines in the presence of SbCl₅.

Since some spectroscopic and analytical data collected for the solid intermediates 3a-c precipitated from the reaction mixture were consistent with the \(N^4,N^4,N^4,N^4\)-tetraalkylbiphenyl-4,4’-diaminium structures (Scheme 4), we carried out some experiments to investigate the nature of that reaction intermediates and to deepen the synthetic applications of such reaction.

First, different experimental conditions have been explored, and the collected data showed that better yields of benzidines 2a-d can be obtained in the presence of stoichiometric amounts of SbCl₅ (Table 2).

Subsequently, we performed some specific coupling experiments to clarify the nature of our reaction intermediates, aimed at definitively exclude the hypothesis of their “aniline” structure (e.g., adduct \(1_{C-Sb}\), Scheme 3) and/or confirming its “benzidinium” nature, as depicted in Scheme 4.

We isolated the two solid-intermediates 3a and 3c from the reaction of SbCl₅ with \(N,N\)-dimethylaniline 1a and \(N,N\)-diisopropylaniline 1c, respectively. Then, equimolecular amounts of 3a and 3c were mixed and heated under reflux in the presence of KOH (Scheme 5).
Table 2. Products and yields of the reaction of \(N,N\)-dialkylanilines (1a-d) with \(\text{SbCl}_5/\text{CH}_2\text{Cl}_2\).\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>(\text{SbCl}_5/\text{PhNR}_2)</th>
<th>Conversion (%)</th>
<th>Yield 2a-d (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me</td>
<td>1:1</td>
<td>100</td>
<td>2a (81)</td>
</tr>
<tr>
<td>2</td>
<td>Me</td>
<td>2:1</td>
<td>100</td>
<td>2a (80)</td>
</tr>
<tr>
<td>3</td>
<td>Me</td>
<td>5:1</td>
<td>100</td>
<td>2a (83)</td>
</tr>
<tr>
<td>4</td>
<td>Me</td>
<td>0.5:1</td>
<td>50</td>
<td>2a (50)</td>
</tr>
<tr>
<td>5</td>
<td>Me</td>
<td>0.2:1</td>
<td>30</td>
<td>2a (24)</td>
</tr>
<tr>
<td>6</td>
<td>Et</td>
<td>1:1</td>
<td>100</td>
<td>2b (84)</td>
</tr>
<tr>
<td>7</td>
<td>Et</td>
<td>0.5:1</td>
<td>50</td>
<td>2b (43)</td>
</tr>
<tr>
<td>8</td>
<td>-(\text{CH}_2)_4-</td>
<td>1:1</td>
<td>40</td>
<td>2d (38)</td>
</tr>
<tr>
<td>9</td>
<td>-(\text{CH}_2)_4-</td>
<td>2:1</td>
<td>70</td>
<td>2d (62)(^b)</td>
</tr>
</tbody>
</table>

\(^a\) The reaction mixtures were stirred for 24 h under nitrogen atmosphere after quenching with aq. \(\text{K}_2\text{CO}_3\) (See Experimental).
\(^b\) 3\% of chlorinated products were also observed.

As a result, only the symmetric benzidines 2a and 2c were obtained (Scheme 5), and no cross-coupling reactions were observed, as expected if the solids 3a and 3c had the adducts 1\(_{\text{C,Sb}}\) structures.

Scheme 5

Next, we studied the reaction between \(N,N\)-diisopropylamine 1c and the solid 3a: this experiment provided the symmetrical substituted benzidine 2a, together with some starting unreacted aniline 1c (Scheme 6).
Scheme 6

Conversely, little amounts of 2f was detected in the reaction of an equimolecular mixture of the two anilines 1a and 1c with SbCl₅, followed by the basic treatment (aq. KOH) (Scheme 7). The different conversion of the two anilines could be due to the different rate of reaction of the starting materials.

Scheme 7

All the results collected in the above described coupling experiments are consistent with the hypothesis that in the reaction with SbCl₅, the C-C formation between the two N,N-dialkylarylamines moieties plausibly takes place before the final basic treatment: consequently, the structure of adduct 1c-Sb (and the following radical intermediate of Scheme 3) are not consistent with the nature of the solid intermediates 3a-d.

Based on the above results, we proposed that the benzidines formation could occur plausibly through a SE mechanism, as hypothesized in Scheme 4, where the dimerization could be explained as the result of a preliminary interaction of SbCl₅ with the arylamine nitrogen of one molecule, followed by the coupling of the 1N-Sb adduct with a second molecule of the starting aniline.

According to that hypothesis, the dimerization step should be rate determining, and a decrease of reactivity should be observed with sterically hindered substrates.

As expected, low reactivity was observed in the reaction of 1-N,N-dimethylnaphthylamine (1g) with SbCl₅ (Scheme 8), probably due to the involvement of two species (naphthylamine and ammonium adduct), both with a hindered α-position.
However, since it has been reported that SbCl$_5$ reacts through the formation of cation-radical intermediates in similar reaction conditions,$^{14}$ a radical mechanism hypothesis could not definitively be excluded. Further investigations are actually in progress on this point, aimed also to a full characterization of the reaction intermediates 3a-c by X-ray crystallography.

**Conclusions**

In conclusion, in this investigation SbCl$_5$ was found to promote oxidative coupling of $N,N$-dialkylarylamines to benzidines. On the basis of specific coupling experiments, and the spectroscopic and analytical data collected for the solid intermediates 3a-c, the benzidines formation could be explained as the result of a preliminary interaction of SbCl$_5$ with the nitrogen atom of one arylamine molecule, followed by the coupling of this $N$-adduct with a second molecule of the starting aniline. However, since SbCl$_5$ reacts through the formation of cation-radical intermediates,$^{14}$ a radical mechanism hypothesis could not definitively be excluded. Further investigations are in progress on this point, aimed to a full characterization of the reaction intermediates 3a-c by X-ray crystallography. Other investigations are also in progress to optimize the yields of the formation of not-symmetrically substituted benzidines and/or other different coupling products.

The oxidative coupling of aniline derivatives here reported provides a new synthetic methodology to $N,N,N',N'$-tetraalkylenbenzidines, that are actually interesting studied and used for their electric conductivity in the field of organic solar cells, photoconductors, oLED and other interesting devices.$^{15-18}$

**Experimental Section**

**General.** Melting points taken on Electrothermal apparatus were uncorrected. $^1$H NMR spectra were recorded on a VARIAN XL-200, a Varian-Mercury 300 MHz, a Varian-Inova-400 MHz, a
Bruker-Aspect 3000 console-500 MHz spectrometers and chemical shifts are reported in parts per million (δ). Absolute values of the coupling constant are reported. FT-IR spectra were recorded on a Perkin-Elmer 681 spectrometer. GC analyses were performed on a HP 6890 model, Series II by using a HP1 column (methyl siloxane; 30 m x 0.32 mm x 0.25 μm film thickness). Analytical thin-layer chromatography (TLC) was carried out on pre-coated 0.25 mm thick plates of Kieselgel 60 F254 visualisation was accomplished by UV light (254 nm) or by I₂ vapour. Column chromatography was conducted by using silica gel 60 with a particle size distribution 40-63 μm and 230-400 ASTM. Petroleum ether refers to the 40–60 °C boiling fraction. GC-MS analyses were performed on HP 5995C model and elemental analyses on an Elemental Analyzer 1106 Carlo Erba instrument. CH₂Cl₂ was distilled from CaH₂ under nitrogen; N,N-dialkylarylamines and all the other chemicals and solvents were commercial grade and used without further purification. Due to its toxicity, SbCl₅ (purchased from Aldrich Chemical Co.) must be handled with extreme caution and with dry utensils. All the operations must be done with care away from water and only in a functioning chemical fume hoods. N,N,N’,N’-tetraalkylbenzidines 2 and the halogenated products of the reactions had analytical and spectroscopic data identical to those of commercially available compounds or previously reported in literature. The percentage of Cl for Elemental Analysis of solids 3a-c was determined by Schöniger method.¹⁹

General Procedure for the synthesis of N,N,N’,N’-tetraalkylbenzidines 2a-d, 2g by reaction of N,N-dialkylarylamines with SbCl₅ and final basic treatment. The amounts of N,N-dialkylarylamine indicated below refer to the reaction of N,N-diethylamine with SbCl₅. See Tables 1 and 2 for other substrate/base ratios and conditions.

To a solution of N,N-dialkylarylamine (1a-g) (0.960 mL, 5 mmol) in freshly distilled CH₂Cl₂ (5 mL) kept at room temperature, a solution of SbCl₅ (0.633 mL, 5 mmol) in CH₂Cl₂ (5 mL) was dropwise added, in a nitrogen-flushed three necked flask equipped with a magnetic stirrer, nitrogen inlet and two dropping funnels. The reaction mixture was stirred for 24 h at room temperature; then, to the formed red suspension, a solution of KOH 1M (10 mmol, 10 mL) was added. The obtained dark reaction mixture was refluxed for 1h at room temperature. The two phases were separated and the aqueous layer was extracted three times with CHCl₃. The combined organic extracts were dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. GC analysis or ¹H NMR spectra were recorded on reaction crude for the determination of the substrate conversion percentages; column chromatography of the residue (alumina or silica gel, petroleum ether/ethyl acetate 19:1 to 7:3) afforded the products depicted in Tables 1-2 and Schemes 1, 5-8.

N,N,N’,N’-Tetramethylbenzidine (2a).¹²,¹³,²⁰ CAS: 366-29-0. 81% yield. Mp 196-197 ºC. IR (νmax, cm⁻¹): 2923, 2853, 2799, 1610, 1508, 1439, 1351, 1226, 1195, 1164, 1062, 943, 806, 510. ¹H NMR (500 MHz, CDCl₃): δH 7.50 (d, 4H, aromatic protons, J 8.8 Hz); 6.84 (d, 4H, aromatic protons, J 8.8 Hz); 3.00 (s, 12H). ¹³C NMR (75 MHz, CDCl₃): δC 149.5, 130.0, 127.2, 113.3, 41.0. MS, m/z (%): 240 (M⁺, 100), 225 (30), 224 (12), 209 (5), 196 (4), 152 (7), 120 (11), 119...
(17), 111 (5), 97 (3), 76 (1), 42 (1). In the reaction crude, 3% of **methylene bis (N,N-dimethylaniline)** was also revealed by GC-MS: MS, m/z (%) 254 (M⁺, 23), 237 (3); 226 (100), 211 (39), 195 (5), 182 (4), 169 (3), 152 (5); 134 (5); 126 (6); 112 (20), 104 (5), 90 (2), 76 (2), 42 (1).

**N,N,N',N'-Tetraethylbenzidine (2b)**. 83% yield. IR (νmax, cm⁻¹): 3038, 2968, 2929, 2876, 1609, 1505, 1392, 1373, 1355, 1262, 1197, 1155, 1074, 1007, 807, 513. ¹H NMR (300 MHz, CDCl₃): δ 7.45 (d, 4H, aromatic protons, J 8.8 Hz); 6.76 (d, 4H, aromatic protons, J 8.8 Hz); 3.40 (q, 8H, J 6.9 Hz): 1.21 (t, 12H, J 6.9 Hz). ¹³C NMR (75 MHz, CDCl₃): δc 146.1, 128.7, 126.9, 112.1, 44.3, 12.6. MS, m/z (%) 296 (M⁺, 100), 282 (19), 281 (82), 252 (14), 251 (11), 238 (10), 237 (50), 209 (12), 208 (12), 196 (4), 152 (7), 120 (11), 119 (17), 111 (5), 97 (3), 76 (1), 42 (1).

**N,N,N',N'-Tetraisopropylbenzidine (2c)**. 63% yield. IR (νmax, cm⁻¹): 3069, 2930, 2872, 1609, 1524, 1484, 1380, 1363, 1330, 1288, 1239, 1187, 1155, 1119, 1052, 1019, 815. ¹H NMR (400 MHz, CDCl₃): δ 7.44 (d, 4H, aromatic protons, J 8.6 Hz); 6.96 (d, 4H, aromatic protons, J 8.6 Hz); 3.81 (m, 4H); 1.25 (d, 24H, J 6.8 Hz). MS, m/z (%) 352 (M⁺, 70), 338 (28), 337(100), 295 (15), 279 (35), 251 (12), 237 (40), 194 (10), 152 (11), 119 (9), 111 (5), 43 (8). Anal. calcd for C₂₄H₃₆N₂: C, 81.76; H, 10.29; N, 7.95. Found: C, 81.45; H, 10.05; N, 7.90.

4,4'-Di(pyrrolidin-1-yl)biphenyl (2d). 38% yield. Dark solid. IR (νmax, cm⁻¹): 3036, 2959, 2829, 1610, 1506, 1484, 1367, 1186, 959, 806. ¹H NMR (400 MHz, CDCl₃): δ 7.44 (d, 4H, aromatic protons, J 8.7 Hz), 6.62 (d, 4H, aromatic protons, J 8.7 Hz), 3.32-3.23 (m, 8H, CH₂), 2.05-1.95 (m, 8H, CH₂); ¹³C NMR (100 MHz, CDCl₃): δc 146.7, 127.2, 112.2, 47.9, 25.7. MS, m/z (%) 292 (M⁺, 100), 291 (33), 263 (6), 249 (4), 236 (4), 222 (3), 208 (4), 194 (3), 193 (3), 165 (4), 152 (7), 146 (9), 145 (9), 124 (3), 118 (6), 97 (5), 89 (3), 76 (3), 136 (5), 43 (8). Anal. calcd for C₂₀H₂₄N₂: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.19; H, 8.05; N, 9.95.

3-Chloro-N,N',N',N'-tetraisopropylbiphenyl-4,4'-diamine (2e). 35% yield. IR (νmax, cm⁻¹): 3031, 2969, 2931, 2872, 1609, 1524, 1484, 1414, 1380, 1366, 1330, 1288, 1239, 1189, 1155, 1120, 1052, 1020, 929, 880, 815, 676. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (d, 1H, aromatic protons, J 2.2 Hz): 7.43 (d, 2H, aromatic protons, J 8.6 Hz); 7.38 (dd, 1H, aromatic protons, J 2.2, 8.3 Hz): 7.27 (d, 2H, aromatic protons, J 8.3 Hz); 6.92 (d, 1H, aromatic protons, J 2.2 Hz); 3.85 (septuplet, 2H, J 6.7 Hz); 3.54 (septuplet, 2H, J 6.4 Hz); 1.27 (d, 12H, J 6.7 Hz); 1.06 (d, 12H, J 6.4 Hz); ¹³C NMR (125 MHz, CDCl₃): δc 147.6, 142.8, 139.1, 137.4, 131.3, 128.2, 127.2, 126.8, 123.9, 118.0, 50.0, 47.5, 21.2, 21.1. MS, m/z (%) 388 (M⁺+2, 13), 386 (M⁺, 70), 373 (35), 371 (100), 331 (10), 329 (30), 315 (7), 313 (19), 287 (4), 285 (9), 273 (12), 271 (33), 229 (3), 228 (3), 193 (4), 186 (4), 178 (4), 152 (4), 136 (5), 43 (8).

N',N'-Diisopropyl-N',N'-dimethylbiphenyl-4,4'-diamine (2f). 7% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.50-7.25 (m, 4H, aromatic protons); 6.72-6.63 (m, 4H, aromatic protons); 3.43 (m, 2H, J 6.8 Hz); 3.00 (s, 6H): 1.20 (d, 12H, J 6.8 Hz). MS, m/z (%) 296 (M⁺, 71), 282 (25), 281 (100), 240 (18), 239 (61), 238 (71), 237 (23), 207 (12), 197 (12), 196 (10), 152 (16), 119 (13), 43(5).
N,N,N’,N’-Tetramethylnaphthydine (2g). 38% yield. Mp 132-134 °C. IR (νmax, cm⁻¹): 3055, 2977, 2935, 2863, 2830, 2784, 1579, 1506, 1453, 1420, 1377, 1322, 1292, 1200, 1181, 1144, 1041, 1022, 940, 845, 772, 579. 1H NMR (400 MHz, CDCl₃): δ n 8.37 (d, 2H, J 8.4 Hz, aromatic protons); 7.47-7.51 (m, 2H, aromatic protons); 7.45 (d, 2H, J 8.4 Hz); 7.41 (d, 2H, J 7.6 Hz); 7.30-7.26 (m, 2H, aromatic protons); 7.19 (d, 2H, J 7.6 Hz); 3.00 (s, 12H); 13C NMR (100 MHz, CDCl₃): δc 150.5, 134.6, 133.4, 128.9, 128.1, 127.5, 125.9, 125.2, 124.4, 113.8, 45.6. MS, m/z (%) 340 (M⁺, 100), 325 (17), 310 (6), 309 (5), 295 (4), 294 (4), 281 (6), 280 (9), 279 (4), 278 (5), 253 (5), 252 (9), 250 (4), 239 (4), 170 (6), 169 (4), 162 (4), 161 (3), 154 (4), 139 (4), 126 (3).

4-Chloro-N,N-dimethylnaphthalen-1-amine (1h). 8% yield. 1H NMR (400 MHz, CDCl₃): δ n 8.37-8.33 (m, 1H, aromatic proton); 7.82 -7.78 (m, 1H, aromatic proton); 7.62-7.45 (m, 2H, aromatic protons); 7.38 (d, 2H, J 8.8 Hz); 3.00 (s, 6H); 13C NMR (100 MHz, CDCl₃): δc 145.5, 134.0, 133.4, 130.5, 128.7, 128.1, 126.7, 126.6, 124.7, 43.0. MS, m/z (%) 207 (M⁺+2, 36), 205 M⁺ (100), 204 (51), 188 (14), 170 (35), 169 (66), 168 (55), 162 (12), 155 (13), 154 (27), 140 (8), 128 (8), 127 (20), 126 (21), 87 (3), 84 (7), 63 (5), 42 (7).

2,4-Dichloro-N,N-dimethylnaphthalen-1-amine (Ii). 5% yield. IR (νmax, cm⁻¹): 3072, 2925, 2861, 2794, 1570, 1561, 1478, 1444, 1380, 1298, 1246, 1209, 1165, 1146, 1055, 962, 849, 854, 782, 763, 722 685, 669, 614. 1H NMR (400 MHz, CDCl₃): δ n 8.41-8.35 (m, 1H, aromatic proton); 8.23-8.17 (m, 1H, aromatic proton); 7.61-7.57 (m, 2H, aromatic protons); 7.51 (s, 1H, aromatic proton); 2.99 (s, 6H); 13C NMR (100 MHz, CDCl₃): δc 145.5, 134.6, 130.6, 129.3, 128.9, 128.3, 127.5, 127.2, 125.2, 124.8, 43.0. MS, m/z (%) 243 (M⁺+4, 13), 241 (M⁺+2, 66), 239 (M⁺, 100), 238 (49), 224 (10), 222 (13), 205 (22), 204 (29), 203 (59), 202 (42), 196 (12), 189 (11), 188 (22), 169 (31), 168 (34), 160 (14), 154 (10), 126 (14), 99 (5), 84 (10), 42 (5). A little amount of 3-chloro-N,N,N’-tetramethyl-1,1'-binaphthyl-4,4'-diamine was also detected by MS, m/z (%) 376 (M⁺+2, 37), 374 (M⁺, 100), 359 (6), 307 (4), 294 (4), 293 (4), 292 (4), 279 (4), 278 (6), 252 (5), 250 (4), 187 (6), 172 (4), 161 (4), 154 (3), 139 (5), 125 (4), 126 (14), 99 (5), 84 (10), 42 (5).

**General Procedure for the isolation of Sb-intermediates 3a-c by reaction of N,N-dialkylarylamines with SbCl₅ (Schemes 5-8).** To a solution of N,N-dialkylarylamine (1a-c) (0.960 mL, 5 mmol) in freshly distilled CH₂Cl₂ (5 mL) kept at 0 °C, a solution of SbCl₅ (0.633 mL, 5 mmol) in CH₂Cl₂ (5 mL) was dropwise added in a nitrogen-flushed three necked flask equipped with a magnetic stirrer, nitrogen inlet and two dropping funnels. The reaction mixture was stirred for 24 h at room temperature, and then the red-coloured solid intermediate precipitated during the reaction was filtered under vacuum and under nitrogen atmosphere, washed with anhydrous CH₂Cl₂, and the solvent residue evaporated under reduced pressure.

**Sb-intermediate (3a).** Mp 156-157 °C (dec. 154 °C). Red powder. IR (νmax, cm⁻¹): 3447, 3072, 2964, 2689, 1619, 1570, 1389, 1221, 978, 829. 1H NMR (200 MHz, CD₂Cl₂): δ n 10.25 (bs, 2H, NH⁺: exchange with D₂O), 7.69-7.59 (m, 8H, aromatic protons); 3.40 (d, 12H, J 4.0 Hz). Anal. calcd for C₁₆H₂₂Cl₁₀N₂Sb₂: C, 22.87; H, 2.64; Cl, 37.7, N, 3.33. Found: C, 22.54; H, 2.68; Cl,
37.28, N, 3.15. Analytical and spectroscopic data of intermediate (3a) are consistent with the \(N^4,N^6,N^4',N^6'\)-tetramethylbiphenyl-4,4'-diaminium structure.

**Sb-intermediate (3b).** Mp (dec.) 160 °C, red powder. IR (\(\nu_{max}\), cm\(^{-1}\)): 3437, 2980, 1620, 1553, 1447, 1214, 1072, 828, 697, 551. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta_H\) 12.30 (bs, 2H, NH\(^+\): exchange with D\(_2\)O); 8.41-7.47 (m, 8H, aromatic protons); 3.39 (m, 8H); 1.01, (t, 6H, \(J = 7.8\) Hz); 0.96 (t, 6H, \(J = 7.3\) Hz); \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta_C\) 138.3, 130.9, 129.4, 124.2, 123.6, 53.1, 10.8. Anal. calcd for C\(_{20}\)H\(_{30}\)Cl\(_{10}\)N\(_2\)Sb\(_2\): C, 26.79; H, 3.37; Cl, 39.55, N, 3.12. Found: C, 26.44; H, 3.68; Cl, 39.28, N, 3.15. Analytical and spectroscopic data of intermediate (3b) are consistent with \(N^4,N^6,N^4',N^6'\)-tetraethylbiphenyl-4,4'-diaminium structure.

**Sb-intermediate (3c).** Mp. 230-233 °C (dec. 180 °C), red powder. IR (\(\nu_{max}\), cm\(^{-1}\)): 3431, 2974, 2685, 1619, 1536, 1450, 1378, 1365, 1162, 1118, 825, 673. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \(\delta_H\) 11.95 (bs, 2H, NH\(^+\): exchange with D\(_2\)O); 7.98-7.95 (d, 4H, aromatic protons); 7.82 -7.79 (d, 4H, aromatic protons); 4.22 (m, 4H); 1.26 (d, 6H, \(J = 7.3\) Hz); \(^13\)C NMR (75 MHz, CDCl\(_3\)): \(\delta_C\) 140.2, 133.3, 128.7, 126.1, 55.8, 19.3, 17.5. Anal. calcd for C\(_{24}\)H\(_{38}\)Cl\(_{10}\)N\(_2\)Sb\(_2\): C, 30.19; H, 4.05; N, 2.95. Found: C, 30.19; H, 4.02; Cl, 37.22, N, 2.94. Found: C, 30.19; H, 4.05; N, 2.95. Analytical and spectroscopic data of intermediate (3c) are consistent with \(N^4,N^4',N^4',N^4'\)-tetraisopropylbiphenyl-4,4'-diaminium structure.

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10. In all the cases an insoluble red-brown powder was early observed after SbCl₅ addition to the aniline solution, which has been isolated by filtration from the reaction mixture before the basic final treatment: some efforts have been made for its characterization after recrystallization, to ascertain unambiguously the reaction mechanism.
